



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>A61L 2/00</b>		<b>A2</b>	(11) International Publication Number: <b>WO 99/03512</b>
			(43) International Publication Date: 28 January 1999 (28.01.99)
(21) International Application Number: PCT/US98/14689		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 16 July 1998 (16.07.98)		<b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>	
(30) Priority Data:			
60/053,322 21 July 1997 (21.07.97) US 08/961,622 31 October 1997 (31.10.97) US 09/028,444 24 February 1998 (24.02.98) US			
(71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).			
(72) Inventors: BOUCHER, Jeffrey, Edward; 9470 Shadyoak Court, Cincinnati, OH 45231 (US). KAIN, Denver, James; 3336 Scioto Drive, Cincinnati, OH 45244 (US). HUTTON, Howard, David; 5745 Jessica Street, Loveland, OH 45140 (US).			
(74) Agents: REED, T., David et al.: The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).			
(54) Title: METHOD FOR SANITIZATION OF SUBSTRATES WITH DETERGENT COMPOSITIONS			
(57) Abstract			
<p>A method for sanitizing a substrate by contacting a microbe containing substrate with a detergent composition for a sufficient time to substantially reduce the amount of microbes on the substrate. Metals, coated metals, plastics, rubber, dishware, countertops, fabric, wood surfaces, and other substrates can be sanitized by applying a light duty detergent composition, preferably a liquid, cream, paste, or gel detergent composition, which comprises an antimicrobial agent such as a surfactant.</p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## METHOD FOR SANITIZATION OF SUBSTRATES WITH DETERGENT COMPOSITIONS

### RELATED APPLICATIONS

This application claims priority under 35 U.S.C. 119(e) to U.S. Provisional Application No. 60/053,322, filed on July 21, 1997, and to co-pending U.S. Application No. 08/961,622, filed October 31, 1997.

### TECHNICAL FIELD

The present invention is in the field of detergent compositions, preferably liquid or gel detergents. More specifically, the invention relates to a method for removing soils and sanitizing (significantly reducing microorganism populations) plastics, dishware, countertops, fabric, wood surfaces, and other substrates by applying a light duty detergent composition, preferably a liquid, cream, paste, or gel detergent composition, which preferably comprises non-quaternary surfactants. This method provides enhanced cleaning coupled with sanitizing, disinfecting, or antibacterial action on the treated surfaces.

### BACKGROUND OF THE INVENTION

Detergents used for washing tableware (i.e., glassware, china, silverware, plastic, etc.) or kitchenware (i.e. cook ware, cutting boards, counter tops, etc.) in the home or institution have long been known. Dishwashing in the seventies is reviewed by Mizuno in Vol. 5, Part III of the Surfactant Science Series, Ed. W.G. Cutler and R.C. Davis, Marcel Dekker, N.Y., 1973. The particular requirements of cleansing tableware and leaving it in a sanitary, essentially soil-free, residue-free state has indeed resulted in so many particular compositions that the body of art pertaining thereto is now recognized as quite distinct from other cleansing product art.

Furthermore, consumers continue to have a great concern with the sanitary conditions in their household. There is perceived to be a real problem with germs in the household, particularly on dishware, food preparation areas, and on equipment used with small children or sick persons.

Consumers continue to experience problems with obtaining adequate antibacterial action on various substrates, including typical kitchen surfaces and dishware. Formulators have experienced difficulties in formulating detergents which both remove soils and reduce the amount of microorganisms on the surface. Typically to accomplish both jobs, consumers have resorted to adding chlorine bleach to the wash water or to wiping the already cleaned surface with a bleach-containing solution for added antibacterial action.

Although chlorine bleach is effective for stain fighting and for antibacterial action, it is not compatible with a variety of detergent ingredients and does little to actually remove soils from the substrate. Moreover, bleach is consider harsh to many surfaces and to consumer's hands and it has an unpleasant odor.

As a consequence to the above-identified problem, there has been a substantial amount of research to develop deterative systems which are stable with a variety of ingredients and which accomplishes both soil removal and sanitization.

Moreover, an important consideration in the development of consumer products effective on both soils and germ removal or kill is the additional costs associated with the inclusion of multiple additives. Accordingly, it is of substantial interest to the manufacturers of detergent products to find a less expensive component which can perform both duties.

#### SUMMARY OF THE INVENTION

By the present invention, it has now been discovered that certain surfactants are stable, perform very well on removing soils, and sanitize when the surfactant is applied without additional water (or with minimum additional water) to a substrate and allowed to remain in contact for a period of time.

Accordingly, the present invention solves the long-standing need for an inexpensive cleaning system which performs efficiently and effectively under soil load conditions and which provides very good antimicrobial action. This, in turn, can lead to healthier family members which can manifest itself in less sick days, less chance for transmittance of disease and fewer trips to a healthcare provider.

The invention herein is a method for sanitizing a microbe containing substrate comprising the steps of:

- a) contacting the substrate with a detergent composition comprising an effective amount of an antimicrobial agent;
- b) allowing the detergent composition to remain in contact with the substrate for a sufficient time to significantly reduce the amount of microbes on the substrate.

In one preferred embodiment of this invention, step b) can be carried out in a conventional microwave oven to activate the antimicrobial action of the detergent composition.

Without intent to limit the types of substrates that may be treated, examples of substrates which can be treated by this method include fabrics, ceramic, porcelain, plastic, dish cloths, cutting boards, surgical/medical equipment, baby bottles, dishware, dentifrice/dentures, wood, food preparation surfaces, sponges, glass, rubber, metal, coated metal (e.g., Teflon®-coated pans) and mixtures thereof.

The method of application can vary significantly. For example, the product can be applied directly to the substrate, sprayed onto the substrate, or spread by an implement (sponge, roller, paper towel, dish cloth, etc.) onto the surface to be treated.

The method herein can be employed to kill or reduce the level of viable microbes which may include any various microorganisms, such as bacteria (gram + or -), viruses (enveloped or unenveloped), parasites, fungi/spores, and other typical household germs commonly found on kitchen surfaces.

All percentages and proportions herein are by weight, and all references cited are hereby incorporated by reference, unless otherwise specifically indicated.

#### DETAILED DESCRIPTION OF THE INVENTION

Definitions - The present detergent compositions comprise an "effective amount" or a "soil and sanitizing amount" of a particularly defined antimicrobial agent which is preferably a surfactant. An "effective amount" or "sanitizing amount" of an antimicrobial agent is any amount capable of measurably improving both soil removal from and sanitization of the substrate, i.e., soiled dishware, when it is washed by the consumer. In general, this amount may vary quite widely.

As used herein the terms "disinfecting", "disinfection", "antibacterial", "germ kill", and "sanitization" are intended to mean killing microbes commonly found in household

kitchens and houses. Examples of various microbes include: germs, bacteria, viruses, parasites, and fungi/spores. Preferably the detergent compositions used herein contact the substrate for a sufficient time to significantly reduce the amount of microbes on the substrate. By "significant reduction" it is meant that at least about 50% of the microbes on the substrate are killed or otherwise rendered inactive, preferably the amount of microbes on the substrate is reduced by at least about 90%, and most preferably the amount of microbes on the substrate is reduced by at least about 99.9%.

Examples of surfactants which are useful antimicrobial agents for use herein include anionic, cationic, nonionic, and amphoteric surfactants. Preferred examples are: alkyl alkoxy sulfates, including alkyl ethoxy sulfates, linear alkyl benzene sulfonates, amine oxides, polyhydroxy fatty acid amides, ethoxylated alcohols, diamines, amides, alkyl polyglucosides, betaines, and mixtures thereof. When the antimicrobial agent is a cationic surfactant it is preferred that the cationic surfactant is not a quaternary ammonium surfactant.

The detergent compositions of the present invention comprise surfactant from about 1% to about 80%, preferably from about 10% to about 70%, more preferably from about 20% to about 60%, and most preferably from about 30% to about 50%, by weight of the total composition.

Typically the "sufficient time" in step b) is at least about 10 seconds, preferably from about 15 seconds to about 2 minutes and more preferably from about 30 seconds to about 1 minute. Longer times, of course, are effective.

It has surprisingly been found that placing the substrate, while it is still in contact with the detergent composition, in a conventional microwave oven and operating the oven for a sufficient time, can enhance the antimicrobial action of the detergent composition. While not wanting to be bound by any one theory, it is believed that the energy imparted to the detergent composition by the microwave radiation within the oven serves to activate and enhance the antimicrobial action of the detergent composition. Microwave ovens suitable for use in the present invention are manufactured by companies such as Litton®, Amana®, Sharp®, General Electric®, and others, and have become ubiquitous in kitchens throughout the industrial world. Microwave ovens can be purchased at any

number of department stores, hardware stores and large variety stores, such as K-Mart® and Wal-Mart®.

By "operating" the microwave oven it is meant that the sufficient time is selected and the microwave oven is turned on for the selected length of time; in all respects, the manufacturers suggested operating instructions and safety precautions should be followed. Depending on the length of time selected for operating the microwave oven, the substrate might be warm and require care when removing it from the oven. A cool down period for the substrate may also be desirable.

To achieve maximum sanitization action, the detergent compositions are preferably applied directly to the substrate with a minimum of water, even more preferably free of added water. Moreover, the substrate should remain in contact with the detergent for a sufficient time before water is added or before the detergent is rinsed away. However, the surface to be treated may be prerinsed or wetted before application of the detergent composition herein as long as no standing water remains. In other words, the surface may be damp but not submerged in water. It is believed that the detergent compositions with the percent surfactant level stated herein have sufficiently high ingredient concentrations to allow for some dilution during use. Of course this depends on the concentration of the active ingredients in the product. Preferably the detergent composition is diluted with less than about 10% water, more preferably less than about 30% water and most preferably less than about 50% water.

In contrast and for comparative purposes, in a typical household kitchen, a sink filled with water and dishes and dosed by an average amount of liquid dishwashing detergent product (4 to 7g, with approximately 10-45% surfactant) will have a total product concentration level of less than 1% in the wash water, i.e., diluted by 99% with water. If the washing is conducted in a rubber tub or large bowl sitting in the sink, the total product concentration is only about 5%, i.e., 95% dilution. Even a sponge which has been soaked in water with detergent applied to the sponge's surface will have a detergent product concentration of only about 10%, i.e. 90% dilution.

Product/Instructions - This invention also encompasses the inclusion of instructions on the use of the detergent composition with the package containing the detergent compositions herein or with other forms of advertising associated with the sale or use of

the detergent compositions. The instructions may be included in any manner typically used by consumer product manufacturing or supply companies. Examples include providing instructions on a label attached to the container holding the composition; on a sheet either attached to the container or accompanying it when purchased; or in advertisements, demonstrations, and/or other written or oral instructions which may be connected to the purchase or use of the detergent compositions.

Specifically the instructions will include a description of the use of the surfactant containing detergent composition in connection with allowing the detergent to remain in contact with the substrate before the addition of a substantial volume of water or before rinsing. The instructions, for instance, may additionally include information relating to the length of contact time; the recommended dosage or amount of treating composition to apply to the substrate, if soaking or rubbing is appropriate; the recommended amount of water, if any, to apply to the substrate before and after treatment; other recommended treatment to accompany the detergent application.

Accordingly, the present invention embraces a product comprising a detergent composition comprising an effective amount of an antimicrobial agent and instructions for using the detergent composition, the instructions include the steps of:

- a) contacting a microbe-containing substrate with the detergent composition; and
- b) allowing the detergent composition to remain in contact with the substrate for a sufficient time to significantly reduce the amount of microbes on the substrate.

Other Ingredients - Detergent ingredients or adjuncts optionally included in the instant compositions can include one or more materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or designed to improve the aesthetics, maintain chemical and physical stability, or ease of manufacture of the compositions. Other adjuncts which can also be included in compositions of the invention at their conventional art-established levels, generally from 0% to about 20% of the composition, preferably at from about 0.1% to about 10%, include one or more processing aids, polymer thickeners, dyes, fillers, enzymes, alkalinity sources, hydrotropes, stabilizers, perfumes, solvents, carriers, baking soda, carbonates, hydrobenzoic acid, dicarboxylic acid, bleach, divalent ions, dispersant polymers, chelants, builders such as citrate and buffers. The composition preferably has a pH of from about 3



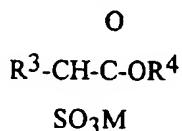
to about 11.5, preferably from about 6 to about 11. The divalent ions, when present, are preferably selected from inorganic cations, organic cations and mixtures thereof, and most preferably are selected from  $Mg^{2+}$ ,  $Ca^{2+}$  and mixtures thereof.

Other non-surfactant germicides may be included for additional antimicrobial action if they do not adversely interfere with the surfactants used herein. Examples of antimicrobials include triclosan, triclocarbon, hydrogen peroxide, other oxygen bleaches, para-chloro-meta-xyleneol, iodine/iodophors, selected alcohols, chlorhexidine, phenols, phospholipids, thymol, eugenol, geraniol, oil of lemon grass, and limonene. Certain quaternary surfactants may also show antimicrobial action and may be included as a secondary germ kill agent.

Anionic Surfactants - The anionic surfactants useful in the present invention are preferably selected from the group consisting of branched alkyl ethoxy sulfates, C<sub>8</sub>-C<sub>18</sub> linear alkylbenzene sulfonate, alpha olefin sulfonate, paraffin sulfonates, methyl ester sulfonates, primary, branched-chain and random C<sub>8</sub>-C<sub>20</sub> alkyl sulfates (AS), the C<sub>8</sub>-C<sub>18</sub> secondary (2,3) alkyl sulfates of the formula  $CH_3(CH_2)_x(CHOSO_3-M^+)CH_3$  and  $CH_3(CH_2)_y(CHOSO_3-M^+)CH_2CH_3$  where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, C<sub>8</sub>-C<sub>18</sub> alkyl alkoxy sulfates ("AE<sub>x</sub>S"; especially EO 0.5-7 ethoxy sulfates), C<sub>8</sub>-C<sub>18</sub> alkyl alkoxy carboxylates (especially the EO 0.5-5 ethoxycarboxylates), the C<sub>8</sub>-C<sub>18</sub> glycerol ethers, the C<sub>8</sub>-C<sub>18</sub> alkyl polyglycosides and their corresponding sulfated polyglycosides, alkyl sulfonates, sarcosinates, taurinates, C<sub>8</sub>-C<sub>18</sub> alpha-sulfonated fatty acid esters and mixtures thereof.

One type of anionic surfactant which can be utilized encompasses alkyl ester sulfonates. These are desirable because they can be made with renewable, non-petroleum resources. Preparation of the alkyl ester sulfonate surfactant component can be effected according to known methods disclosed in the technical literature. For instance, linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids can be sulfonated with gaseous SO<sub>3</sub> according to "The Journal of the American Oil Chemists Society," 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm, and coconut oils, etc.

The preferred alkyl ester sulfonate surfactant comprises alkyl ester sulfonate surfactants of the structural formula:



wherein  $\text{R}^3$  is a  $\text{C}_8\text{-C}_{20}$  hydrocarbyl, preferably an alkyl, or combination thereof,  $\text{R}^4$  is a  $\text{C}_1\text{-C}_6$  hydrocarbyl, preferably an alkyl, or combination thereof, and M is a soluble salt-forming cation. Suitable salts include metal salts such as sodium, potassium, and lithium salts, and substituted or unsubstituted ammonium salts, such as methyl-, dimethyl-, trimethyl-, and quaternary ammonium cations, e.g. tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines, e.g. monoethanol-amine, diethanolamine, and triethanolamine. Preferably,  $\text{R}^3$  is  $\text{C}_{10}\text{-C}_{16}$  alkyl, and  $\text{R}^4$  is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein  $\text{R}^3$  is  $\text{C}_{14}\text{-C}_{16}$  alkyl.

Alkyl sulfate surfactants are another type of surfactant for use herein. Examples of alkyl sulfates are water soluble salts or acids of the formula  $\text{ROSO}_3\text{M}$  wherein R preferably is a  $\text{C}_{10}\text{-C}_{24}$  hydrocarbyl, preferably an alkyl or hydroxyalkyl having a  $\text{C}_{10}\text{-C}_{20}$  alkyl component, more preferably a  $\text{C}_{12}\text{-C}_{18}$  alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali or alkaline (Group IA or Group IIA) metal cation (e.g., sodium, potassium, lithium, magnesium, calcium), substituted or unsubstituted ammonium cations such as methyl-, dimethyl-, and trimethyl ammonium and quaternary ammonium cations, e.g., tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines such as ethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and the like. Typically, alkyl chains of  $\text{C}_{12}\text{-C}_{16}$  are preferred for lower wash temperatures (e.g., below about  $50^\circ\text{C}$ ) and  $\text{C}_{16}\text{-C}_{18}$  alkyl chains are preferred for higher wash temperatures (e.g., above about  $50^\circ\text{C}$ ).

Alkyl alkoxyated sulfate surfactants are another category of useful anionic surfactant. These surfactants are water soluble salts or acids typically of the formula  $\text{RO(A)}_m\text{SO}_3\text{M}$  wherein R is an unsubstituted  $\text{C}_{10}\text{-C}_{24}$  alkyl or hydroxyalkyl group having a  $\text{C}_{10}\text{-C}_{24}$  alkyl component, preferably a  $\text{C}_{12}\text{-C}_{20}$  alkyl or hydroxyalkyl, more preferably  $\text{C}_{12}\text{-C}_{18}$  alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater

than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Exemplary surfactants are C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (1.0) sulfate, C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (2.25) sulfate, C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (3.0) sulfate, and C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (4.0) sulfate wherein M is conveniently selected from sodium and potassium. Surfactants for use herein can be made from natural or synthetic alcohol feedstocks. Chain lengths represent average hydrocarbon distributions, including branching.

Other anionic surfactants useful for deterative and sanitization purposes can also be included in the compositions hereof. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C<sub>9</sub>-C<sub>20</sub> linear alkylbenzene sulphonates, C<sub>8</sub>-C<sub>22</sub> primary or secondary alkanesulphonates, C<sub>8</sub>-C<sub>24</sub> olefin sulphonates, sulphonated polycarboxylic acids prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isothionates such as the acyl isothionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C<sub>6</sub>-C<sub>14</sub> diesters), N-acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula  $RO(CH_2CH_2O)_kCH_2COO-M^+$  wherein R is a C<sub>8</sub>-C<sub>22</sub> alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation, and fatty acids esterified with isethionic acid and neutralized with sodium hydroxide. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A

variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

Nonionic Detergent Surfactants - Suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, at column 13, line 14 through column 16, line 6, incorporated herein by reference. Exemplary, non-limiting classes of useful nonionic surfactants include: C<sub>8</sub>-C<sub>18</sub> alkyl ethoxylates ("AE"), with EO about 1-22, including the so-called narrow peaked alkyl ethoxylates and C<sub>6</sub>-C<sub>12</sub> alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), alkyl dialkyl amine oxide, alkanoyl glucose amide, and mixtures thereof.

Other nonionic surfactants for use herein include:

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal® CO-630, marketed by the GAF Corporation; and Triton® X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company. These compounds are commonly referred to as alkyl phenol alkoxyates, (e.g., alkyl phenol ethoxylates).

The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 10 to about 20 carbon atoms with from about 2 to about 18 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol® 15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear secondary alcohol with 9 moles ethylene oxide), Tergitol® 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol® 45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of

ethylene oxide), Neodol® 23-6.5 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 6.5 moles of ethylene oxide), Neodol® 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol® 45-4 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro® EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company. Other commercially available nonionic surfactants include Dobanol 91-8® marketed by Shell Chemical Co. and Genapol UD-080® marketed by Hoechst. This category of nonionic surfactant is referred to generally as "alkyl ethoxylates."

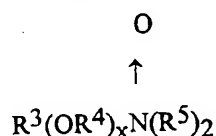
The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic® surfactants, marketed by BASF.

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic® compounds, marketed by BASF.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and

hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein  $\text{R}^3$  is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms;  $\text{R}^4$  is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof;  $x$  is from 0 to about 3; and each  $\text{R}^5$  is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The  $\text{R}^5$  groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

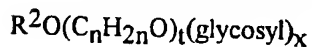
These amine oxide surfactants in particular include  $\text{C}_{10}$ - $\text{C}_{18}$  alkyl dimethyl amine oxides and  $\text{C}_8$ - $\text{C}_{12}$  alkoxy ethyl dihydroxy ethyl amine oxides.

Alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be,

e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

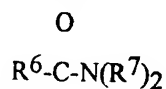
Optionally, and less desirably, there can be a polyalkylene-oxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyl, decyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-sides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-sides and tallow alkyl tetra-, penta-, and hexa-glucosides.

The preferred alkylpolyglycosides have the formula



wherein  $R^2$  is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms;  $n$  is 2 or 3, preferably 2;  $t$  is from 0 to about 10, preferably 0; and  $x$  is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly the 2-position.

Fatty acid amide surfactants having the formula:



wherein  $R^6$  is an alkyl group containing from about 7 to about 21 (preferably from about 9 to about 17) carbon atoms and each  $R^7$  is selected from the group consisting of

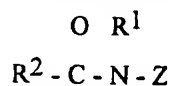
hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl, and -(C<sub>2</sub>H<sub>4</sub>O)<sub>x</sub>H where x varies from about 1 to about 3.

Preferred amides are C<sub>8</sub>-C<sub>20</sub> ammonia amides, monoethanolamides, diethanolamides, and isopropanolamides.

Cationic/amphoteric - Non-quaternary, cationic deterative surfactants can also be included in detergent compositions of the present invention. Cationic surfactants useful herein are described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980.

Ampholytic surfactants can be incorporated into the detergent compositions hereof. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35 for examples of ampholytic surfactants. Preferred amphoteric include C<sub>12</sub>-C<sub>18</sub> alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C<sub>6</sub>-C<sub>12</sub> alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, and mixtures thereof.

Polyhydroxy Fatty Acid Amide Surfactant - The detergent compositions hereof may also contain polyhydroxy fatty acid amide surfactant. The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:



wherein: R<sup>1</sup> is H, C<sub>1</sub>-C<sub>4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C<sub>1</sub>-C<sub>4</sub> alkyl, more preferably C<sub>1</sub> or C<sub>2</sub> alkyl, most preferably C<sub>1</sub> alkyl (i.e., methyl); and R<sup>2</sup> is a C<sub>5</sub>-C<sub>31</sub> hydrocarbyl, preferably straight chain C<sub>7</sub>-C<sub>19</sub> alkyl or alkenyl, more preferably straight chain C<sub>9</sub>-C<sub>17</sub> alkyl or alkenyl, most preferably straight chain C<sub>11</sub>-C<sub>15</sub> alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z



preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of  $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$ ,  $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$ , and alkoxylated derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein n is 4, particularly  $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$ .

R' can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

$\text{R}^2\text{-CO-N<}$  can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

Diamines - Preferred organic diamines are those in which pK1 and pK2 are in the range of about 8.0 to about 11.5, preferably in the range of about 8.4 to about 11, even more preferably from about 8.6 to about 10.75. Preferred materials for performance and

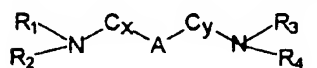
supply considerations are 1,3 propane diamine (pK1=10.5; pK2=8.8), 1,6 hexane diamine (pK1=11; pK2=10), 1,3 pentane diamine (Dytek EP) (pK1=10.5; pK2=8.9), 2-methyl 1,5 pentane diamine (Dytek A) (pK1=11.2; pK2=10.0). Other preferred materials are the primary/primary diamines with alkylene spacers ranging from C4 to C8.

Definition of pK1 and pK2 - As used herein, "pKa1" and "pKa2" are quantities of a type collectively known to those skilled in the art as "pKa". pKa is used herein in the same manner as is commonly known to people skilled in the art of chemistry. Values referenced herein can be obtained from literature, such as from "Critical Stability Constants: Volume 2, Amines" by Smith and Martell, Plenum Press, NY and London, 1975. Additional information on pKa's can be obtained from relevant company literature, such as information supplied by Dupont, a supplier of diamines.

As a working definition herein, the pKa of the diamines is specified in an all-aqueous solution at 25°C and for an ionic strength between 0.1 to 0.5 M. The pKa is an equilibrium constant which can change with temperature and ionic strength; thus, values reported in the literature are sometimes not in agreement depending on the measurement method and conditions. To eliminate ambiguity, the relevant conditions and/or references used for pKa's of this invention are as defined herein or in "Critical Stability Constants: Volume 2, Amines". One typical method of measurement is the potentiometric titration of the acid with sodium hydroxide and determination of the pKa by suitable methods as described and referenced in "The Chemist's Ready Reference Handbook" by Shugar and Dean, McGraw Hill, NY, 1990.

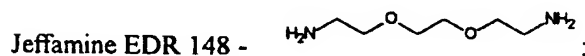
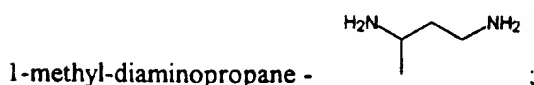
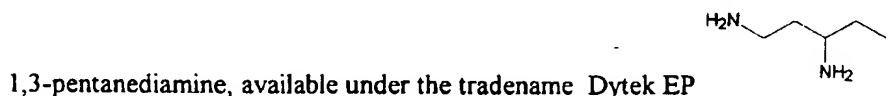
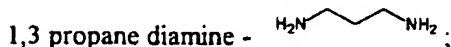
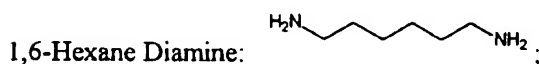
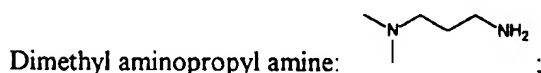
It has been determined that substituents and structural modifications that lower pK1 and pK2 to below about 8.0 are undesirable and cause losses in performance. This can include substitutions that lead to ethoxylated diamines, hydroxy ethyl substituted diamines, diamines with oxygen in the beta (and less so gamma) position to the nitrogen in the spacer group (e.g., Jeffamine EDR 148). In addition, materials based on ethylene diamine are unsuitable.

The diamines useful herein can be defined by the following structure:



wherein  $R_{1-4}$  are independently selected from H, methyl,  $-CH_2CH_3$ , and ethylene oxides;  $C_x$  and  $C_y$  are independently selected from methylene groups or branched alkyl groups where  $x+y$  is from about 3 to about 6; and A is optionally present and is selected from electron donating or withdrawing moieties chosen to adjust the diamine pKa's to the desired range. If A is present, then x and y must both be 1 or greater.

Examples of preferred diamines include the following:

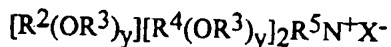


and mixtures thereof.

Secondary Surfactants - Secondary deterative surfactant can be selected from quaternary ammonium surfactants as long as the quaternary surfactant does not adversely affect the primary surfactant of this invention. Generally, the secondary, quaternary

surfactant may be added for additional antimicrobial action in the detergent compositions herein.

Quaternary surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula:



wherein  $R^2$  is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each  $R^3$  is selected from the group consisting of  $-CH_2CH_2-$ ,  $-CH_2CH(CH_3)-$ ,  $-CH_2CH(CH_2OH)-$ ,  $-CH_2CH_2CH_2-$ , and mixtures thereof; each  $R^4$  is selected from the group consisting of  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl, benzyl, ring structures formed by joining the two  $R^4$  groups,  $-CH_2CHOHCHOHCOR^6CHOH-CH_2OH$  wherein  $R^6$  is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when  $y$  is not 0;  $R^5$  is the same as  $R^4$  or is an alkyl chain wherein the total number of carbon atoms of  $R^2$  plus  $R^5$  is not more than about 18; each  $y$  is from 0 to about 10 and the sum of the  $y$  values is from 0 to about 15; and  $X$  is any compatible anion.

**Builders** - Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. The level of builder can vary widely depending upon the end use of the composition and its desired physical form. Liquid formulations may comprise from about 1% to about 50%, more typically about 2% to about 30%, by weight, of detergent builder.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders are disclosed in Berg, U.S.

Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of importance for liquid detergent formulations due to their availability from renewable resources and their biodegradability. Oxy-disuccinates are also especially useful in such compositions and combinations.

Also suitable in the compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C<sub>12</sub>-C<sub>18</sub> monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates.

Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Examples of silicate builders are the alkali metal silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst

(commonly abbreviated herein as "SKS-6"). NaSKS-6 can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms.

Useful aluminosilicate ion exchange materials are commercially available. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976.

Enzymes - Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active bleach, detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as dishware and the like. In practical terms for current commercial preparations, the compositions herein may comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

The preparation of protease enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a

protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

Amylases suitable herein, especially for, but not limited to automatic dishwashing purposes, include, for example,  $\alpha$ -amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp 6518-6521 Preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994. Other amylases include variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo.

Cellulases usable herein include those disclosed in U.S. 4,435,307, Barbesgoard et al, March 6, 1984. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® (Novo) is especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Enzyme Stabilizing System - Enzyme-containing, including but not limited to, liquid compositions, herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition. See Severson, U.S. 4,537,706 for a review of Borate stabilizers.

Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite,

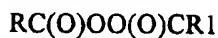


thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired.

#### Bleaching Agents

Suitable bleaching for possible use herein are listed below:

Diacyl Peroxide Bleaching Species - The composition of the present invention may contain diacyl peroxide of the general formula:



wherein R and R<sub>1</sub> can be the same or different and are hydrocarbyls, preferably no more than one is a hydrocarbyl chain of longer than ten carbon atoms, more preferably at least one has an aromatic nucleus.

Examples of suitable diacyl peroxides are selected from the group consisting dibenzoyl peroxide, dianisoyl peroxide, benzoyl gluaryl peroxide, benzoyl succinyl peroxide, di-(2-methylbenzoyl) peroxide, dipthaloyl peroxide, dinaphthoyl peroxide, substituted dinaphthoyl peroxide, and mixtures thereof, more preferably dibenzoyl peroxide, dicumyl peroxide, dipthaloyl peroxides and mixtures thereof. A particularly preferred diacyl peroxide is dibenzoyl peroxide.

Hydrogen Peroxide Source - The compositions of the present invention may comprise a source of oxygen bleach, preferably a source of hydrogen peroxide with or without a selected bleach activator. The source of hydrogen peroxide is typically any common hydrogen-peroxide releasing salt, such as sodium perborate or sodium percarbonate. Hydrogen peroxide sources include the various forms of sodium perborate and sodium percarbonate and modified forms. An "effective amount" of a source of hydrogen peroxide is any amount capable of measurably improving stain removal (especially of tea and tomato stains) from the soiled substrate compared to a hydrogen peroxide source-free composition when the soiled substrate is washed by the consumer.

The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxy-hydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

Another source of hydrogen peroxide is enzymes. Examples include Lipoxidase, glucose oxidase, peroxidase, alcohol oxidases, and mixtures thereof.

Bleach Activators - Numerous conventional bleach activators are known. See for example activators referenced hereinabove in the background as well as U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. Nonanoyloxybenzenesulfonate (NOBS) or acyl lactam activators may be used, and mixtures thereof with TAED can also be used. See also U.S. 4,634,551 for other typical conventional bleach activators. Also known are amido-derived bleach activators of the formulae:  $R^1N(R^5)C(O)R^2C(O)L$  or  $R^1C(O)N(R^5)R^2C(O)L$  wherein  $R^1$  is an alkyl group containing from about 6 to about 12 carbon atoms,  $R^2$  is an alkylene containing from 1 to about 6 carbon atoms,  $R^5$  is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. Further illustration of bleach activators of the above formulae include (6-octanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)-oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551. Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990. Still another class of bleach activators includes acyl lactam activators such as octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethyl-hexanoyl valerolactam, t-butylbenzoylcaprolactam, t-butylbenzoylvalerolactam and mixtures thereof. The present compositions can optionally comprise aryl benzoates, such as phenyl benzoate, and acetyl triethyl citrate.

Quaternary Substituted Bleach Activators - The present compositions can also comprise quaternary substituted bleach activators (QSBA). QSBA's herein typically have the formula  $E-[Z]_n-C(O)-L$ , wherein group E is referred to as the "head", group Z is referred to as the "spacer" (n is 0 or 1, i.e., this group may be present or absent, though its presence is generally preferred) and L is referred to as the "leaving group". These compounds generally contain at least one quaternary substituted nitrogen moiety, which can be contained in E, Z or L. More preferably, a single quaternary nitrogen is present and it is located in group E or group Z. In general, L is a leaving group, the pKa of the corresponding carbon acid (HL) of which can lie in the general range from about 5 to about 30, more preferably, from about 10 to about 20, depending upon the hydrophilicity of the QSBA. pKa's of leaving groups are further defined in U.S. Pat. No. 4,283,301. Leaving groups and solubilizing tendencies of quaternary moieties which can be present in the QSBA's are further illustrated in U.S. 4,539,130, Spt. 3, 1985 incorporated by reference.

British Pat. 1,382,594, published Feb. 5, 1975, discloses a class of QSBA's found suitable for use herein. U.S. 4,818,426 issued Apr. 4., 1989 discloses another class of QSBA's suitable for use herein. See, for example, U.S. 5,093,022 issued March 3, 1992 and U.S. 4,904,406, issued Feb. 27, 1990. Additionally, QSBA's are described in EP 552,812 A1 published July 28, 1993, and in EP 540,090 A2, published May 5, 1993.

Chlorine Bleach - Any chlorine bleach typically known in the art is suitable for use herein. Preferred chlorine bleaches for use herein include sodium hypochlorite, lithium hypochlorite, calcium hypochlorite, chlorinated trisodium phosphates, and mixtures thereof. For more about chlorine bleaches see *Surfactant Science Series*, Vol. 5, Part II, pages 520-26.

Bleach catalysts - If desired, detergent compositions herein may additionally incorporate a catalyst or accelerator to further improve bleaching or starchy soil removal. Any suitable bleach catalyst can be used. The compositions will comprise from about 0.0001% to about 0.1% by weight of bleach catalyst.

Typical bleach catalysts those disclosed in U.S. Pat. 4,810,410 to Diakun et al, issued March 7, 1989. The active species thereof is believed to be  $\{Co(NH_3)_5(OOH)\}^{2+}$  and is disclosed in J. Chem. Soc. Faraday Trans., 1994, Vol. 90, 1105-1114. Other

catalysts include manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. 5,244,594; U.S. 5,194,416; U.S. 5,114,606; and EP Nos. 549,271 A1, 549,272 A1, 544,440 A2, and 544,490 A1. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

Transition metals may be precomplexed or complexed *in-situ* with suitable donor ligands selected in function of the choice of metal, its oxidation state and the denticity of the ligands. Other complexes which may be included herein are those of U.S. Application Ser. No. 08/210,186, filed March 17, 1994.

Perfumes - Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 4%, by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Material Care Agents - The present compositions may optionally contain as corrosion inhibitors and/or anti-tarnish aids one or more material care agents such as silicates. Material care agents include bismuth salts, transition metal salts such as those of manganese, certain types of paraffin, triazoles, pyrazoles, thiols, mercaptans, aluminium fatty acid salts, and mixtures thereof and are preferably incorporated at low levels, e.g., from about 0.01% to about 5% of the composition. A preferred paraffin oil is a predominantly branched aliphatic hydrocarbon comprising from about 20 to about 50 carbon atoms with a ratio of cyclic to noncyclic hydrocarbons of about 32 to 68 sold by Wintershall, Salzbergen, Germany as WINOG 70®.  $\text{Bi}(\text{NO}_3)_3$  may be added. Other corrosion inhibitors are illustrated by benzotriazole, thiols including thionaphthol and

thioanthranol, and finely divided aluminium fatty acid salts. All such materials will generally be used judiciously so as to avoid producing spots or films on glassware or compromising the bleaching action of the compositions. For this reason, it may be preferred to formulate without mercaptan anti-tarnishes which are quite strongly bleach-reactive or common fatty carboxylic acids which precipitate with calcium.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-triacetates, ethylenediamine tetrapropionates, triethylenetetra-amine-hexacetates, diethylene-triaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene. A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although

others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are

known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Other polymeric materials which can be included are polypropylene glycol (PPG), propylene glycol (PG), and polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

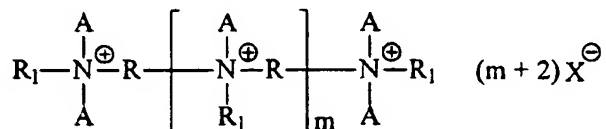
Alkoxyated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula  $-(CH_2CH_2O)_m(CH_2)_nCH_3$  wherein  $m$  is 2-3 and  $n$  is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxyated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Another polymer dispersant form use herein includes polyethoxylated-polyamine polymers (PPP). The preferred polyethoxylated-polyamines useful herein are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's). A common polyalkyleneamine (PAA) is tetrabutyleneamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines,

i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

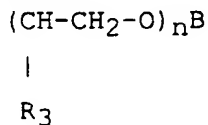
Polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

Additionally, certain alkoxylated (especially ethoxylated) quaternary polyamine dispersants are useful herein as dispersants. The alkoxylated quaternary polyamine dispersants which can be used in the present invention are of the general formula:



where R is selected from linear or branched C<sub>2</sub>-C<sub>12</sub> alkylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene, C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, [(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>CH<sub>2</sub>CH<sub>2</sub>]- and -CH<sub>2</sub>CH(OH)CH<sub>2</sub>O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>CH<sub>2</sub>CH(OH)CH<sub>2</sub>]- where q is from about 1 to about 100. If present, Each R<sub>1</sub> is independently selected from C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>7</sub>-C<sub>12</sub> alkylaryl, or A. R<sub>1</sub> may be absent on some nitrogens; however, at least three nitrogens must be quaternized.

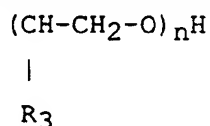
A is of the formula:





where  $R_3$  is selected from H or  $C_1$ - $C_3$  alkyl,  $n$  is from about 5 to about 100 and B is selected from H,  $C_1$ - $C_4$  alkyl, acetyl, or benzoyl;  $m$  is from about 0 to about 4, and X is a water soluble anion.

In preferred embodiments, R is selected from  $C_4$  to  $C_8$  alkylene,  $R_1$  is selected from  $C_1$ - $C_2$  alkyl or  $C_2$ - $C_3$  hydroxyalkyl, and A is:



where  $R_3$  is selected from H or methyl, and  $n$  is from about 10 to about 50; and  $m$  is 1.

In another preferred embodiment R is linear or branched  $C_6$ ,  $R_1$  is methyl,  $R_3$  is H, and  $n$  is from about 20 to about 50, and  $m$  is 1.

The levels of these dispersants used can range from about 0.1% to about 10%, typically from about 0.4% to about 5%, by weight. These dispersants can be synthesized following the methods outline in US. Patent No. 4,664,848, or other ways known to those skilled in the art.

**Hydrotropes** - Hydrotropes suitable for use in the compositions herein include  $C_1$ - $C_3$  alkyl aryl sulfonates,  $C_6$ - $C_{12}$  alkanols,  $C_1$ - $C_6$  carboxylic sulfates and sulfonates, urea, hydrocarboxylates,  $C_1$ - $C_4$  carboxylates, organic diacids, and mixtures thereof.

Suitable  $C_1$ - $C_3$  alkyl aryl sulfonates include sodium, potassium, calcium, and ammonium xylene sulfonates, toluene sulfonates, cumene sulfonates, and naphthalene sulfonates.

**Divalent Ions** - Compositions of this invention herein optionally, but preferably, contain magnesium and or calcium ions to aid in good grease removal and improved storage stability. These ions can be present in the compositions herein at an active level of from about 0.1% to about 4%, by weight.

**Thickeners** - Thickeners for use herein can be selected from clay, polycarboxylates, such as Polygel<sup>®</sup>, gums, carboxymethyl cellulose, polyacrylates, polyvinylpyrrolidone, polyamide resins, titanium dioxide, fumed silica, and mixtures thereof.

One preferred clay type herein has a double-layer structure. The clay may be naturally occurring, e.g., Bentonites, or artificially made, e.g., Laponite<sup>®</sup>. Laponite<sup>®</sup> is

supplied by Southern Clay Products, Inc. See *The Chemistry and Physics of Clays*, Grimshaw, 4th ed., 1971, pages 138-155, Wiley-Interscience.

Another preferred thickener for use in the present invention is hydroxypropyl methylcellulose.

Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid, and methylenemalononic acid. Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. See for example, Diehl, U.S. Pat. 3,308,067, March 7, 1967.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

Non-Aqueous Liquid Detergents - The manufacture of liquid detergent compositions which comprise a non-aqueous carrier medium can be prepared according to the disclosures of U.S. Patents 4,753,570; 4,767,558; 4,772,413; 4,889,652; 4,892,673; GB-A-2,158,838; GB-A-2,195,125; GB-A-2,195,649; U.S. 4,988,462; U.S. 5,266,233; EP-A-225,654 (6/16/87); EP-A-510,762 (10/28/92); EP-A-540,089 (5/5/93); EP-A-540,090 (5/5/93); U.S. 4,615,820; EP-A-565,017 (10/13/93); EP-A-030,096 (6/10/81), incorporated herein by reference. Such compositions can contain various particulate deterative ingredients (e.g., bleaching agents, as disclosed hereinabove) stably suspended therein. Such non-aqueous compositions thus comprise a LIQUID PHASE and, optionally but preferably, a SOLID PHASE, all as described in more detail hereinafter and in the cited references.

Aside from sanitizing as discussed above, the compositions of this invention can be used to form aqueous washing solutions for use in hand dishwashing. Generally, an effective amount of such compositions is added to water to form such aqueous cleaning

or soaking solutions. The aqueous solution so formed is then contacted with the dishware, tableware, and cooking utensils.

An effective amount of the detergent compositions herein added to water to form aqueous cleaning solutions can comprise amounts sufficient to form from about 500 to 20,000 ppm of composition in aqueous solution. More preferably, from about 500 to 5,000 ppm of the detergent compositions herein will be provided in aqueous cleaning liquor.

The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

In the following Examples all levels are quoted as % by weight of the composition.

#### EXAMPLE I

<u>Ingredient</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
Na AExS (x is 0.5)	33	30	33	36	26	31
Amine Oxide	5	6	5	5	2	4.5
Polyhydroxy fatty acid amide	4	4	4	2	1	4
C11E9 nonionic	1	1	1	1	5	1
Betaine					2	
Ethanol	5	5	5	5	6	5
DTPA	0.1	0.1	0.1	0.1	-	0.1
MgCl <sub>2</sub>	3	3	3	3	-	-
Hydrotrope	5	5	5	5	2	5
Na <sub>2</sub> SO <sub>4</sub>	0.2	0.15	0.2	0.2	0.2	0.15
Hydrogen peroxide	0.05	0.05	0.05	0.05	-	0.05
Thickener	-	-	0.5	0.5	-	1.4
Potassium Carbonate	-	-	-	-	-	3
Potassium Chloride	-	-	-	-	-	3
Balance (water, unreacted, filler, etc.)	to 100%	to 100%	to 100%	to 100%	to 100%	to 100%
pH (10%)	7.5	7.5	7.4	7.5	8	10.5

<u>Ingredient</u>	<u>G</u>	<u>H</u>
Na AExS	33	22
Amine Oxide	6	-
Pentane/Hexane Diamine	7	-
Linear Alkyl Benzene Sulfonate	-	13
Methyl ethanolamine	-	1.5
Alkyl polyglucoside	-	11
C11E9 nonionic	5	-
Ethanol	5	4.5
DTPA	0.1	-
Hydrotrope	-	2.5
Hydrogen peroxide	0.03	-
Na <sub>2</sub> SO <sub>4</sub>	0.2	-
Thickener	0.5	-
Balance (water, unreacted, filler, etc.)	to 100%	to 100%

DTPA is ethylenediaminetetracetate.

Hydrotropes can be selected from calcium, sulfate or sodium xylene sulfonates and toluene sulfonates.

Thickeners include Tetronic™ and Accusol™.

The formulas provide significant germ kill (*Escherichia coli* and *Staphylococcus aureus*) when applied to a surface and allowed to remain in contact with the surface for at least 15 seconds before rinsing.

What is claimed is:

1. A method for sanitizing a microbe containing substrate characterized by the steps of:
  - a) contacting the substrate with a detergent composition characterized by an effective amount of an antimicrobial agent; and
  - b) allowing the detergent composition to remain in contact with the substrate for a sufficient time to significantly reduce the amount of microbes on the substrate.
2. A method according to claim 1, wherein the antimicrobial agent is a surfactant selected from the group consisting of anionic, nonionic, cationic, amphoteric surfactants, and mixtures thereof.
3. A method according to claim 2, wherein the surfactant comprises from about 1% to about 80%, by weight of the detergent composition.
4. A method according to claim 1, wherein the substrate is constructed of a material selected from the group consisting of metal, coated metal, ceramic, porcelain, plastic, rubber, sponge, fabric, wood, glass, and mixtures thereof.
5. A method according to claim 1, wherein the detergent composition further comprises one or more detergent adjuvants selected from the group consisting of processing aids, polymer thickeners, dyes, fillers, enzymes, alkalinity sources, hydrotropes, stabilizers, perfumes, solvents, carriers, baking soda, carbonates, hydrobenzoic acid, dicarboxylic acid, bleach, divalent ions, dispersant polymers, chelants, builders, buffers, and mixtures thereof.
6. An antimicrobial product characterized by:
  - a detergent composition characterized by an effective amount of an antimicrobial agent; and
  - instructions for using the detergent composition;wherein the instructions include the steps of:
  - a) contacting a microbe containing substrate with the detergent composition; and
  - b) allowing the detergent composition to remain in contact with the substrate for a sufficient time to significantly reduce the amount of microbes on the substrate.

7. A method according to claim 1, wherein the detergent composition is applied with no more than 50% dilution with water.
8. A method according to claim 1, wherein the substrate is selected from the group consisting of dishware, dish cloths, cutting boards, sponges, dentifrice/dentures, food preparation surfaces, surgical/medical equipment, baby bottles and mixtures thereof.
9. A method for sanitizing a microbe containing substrate characterized by the steps of:
  - a) contacting the substrate with a detergent composition comprising an effective amount of an antimicrobial agent;
  - b) while the detergent composition and the substrate are still in contact, placing the substrate in a microwave oven;
  - c) operating the microwave oven for a sufficient time to significantly reduce the amount of microbes on the substrate.
10. A product according to claim 6, wherein step b) further comprises the following instructions: the substrate may optionally be placed in a microwave oven, and the microwave oven operated for the sufficient time.